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Statistical Mechanics For Calculation of Thermal Magnetic Electrical and Mechanical Properties of Materials

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Preface

Our work during the period covered by this report was devoted to the properties of materials using methods of statistical mechanics.

The main focus of our research was in the following areas:

I. Kinetics of quenched alloys.

II. Phase diagrams of alloys.

III. Equilibrium and kinetic properties of polymers.

IV. Properties of simple fluids and electrolytes.

Our work involved both theoretical studies and computer simulations of model systems. These simulations, which were among the largest of their kind, greatly contributed to our understanding of the microscopic processes involved in various macroscopic phenomena.

I. ALLOYS

1. Kinetics of Phase Transformations in Quenched Alloys.

During the whole period covered by this report we were engaged in a multifaceted study of the time evolution of quenched binary (A-B) alloys. At sufficiently high temperatures all alloys exist in a single phase disordered state. At low temperatures, they generally exist in ordered states. The nature of the ordered states depends on whether it is preferable (energetically) for the particles of each species to be surrounded by their own kind or by the different species: examples of such systems are ZnAl and CuPd, respectively. These states are analogous to the

ferromagnetic and anti-ferromagnetic states in magnetic systems.

The question of interest is how does an alloy which is suddenly cooled (quenched), so that the atoms have no time to migrate during the quench, evolve in time (following the quench) from the homogeneous disordered state it finds itself in to the equilibrium phase appropriate for it at the low temperature; phase-segregated or ordered. This is a problem of practical importance to the metallurgist since properties of many alloys such as their strength, ductility, etc. depend on their structure. This in turn is greatly influenced by the heat treatment the material undergoes. An understanding of the kinetics of such processes should thus aid in the development of materials with desirable properties.

a) Segregating Alloys

We studied the structure functions $S(k,t)$ obtained from computer simulations of the time evolution of a segregating binary alloy following quenching into the immiscibility gap. Our most important finding was that $S(k,t)$ has a simple scaling behavior, $S(k,t) \sim K^3(t)F(k/K(t))$ at late times. The shape of the function $F(x)$ depends somewhat on the part of the coexistence region into which the quench is made. Comparison with experiments on quenched alloys and also binary liquids is quite satisfactory. In fact most experimentalists now use our results as a standard of comparison for analyzing their data: see publication [25] for the most complete description of our results.

We also studied the time evolution of the "grains", i.e. clumps of precipitate of the minority phase, following quenching. Some features of the size distribution of the grains were found to satisfy theoretical predictions others did not. The relation between grain size distribution and structure function were investigated and some aspects clarified. Further theoretical and computer experiments are needed to obtain a full understanding of the coarsening process.

b) Ordering Alloys

Alloys which form ordered superlattices at low temperatures are described quantitatively by a long-range-order parameter η_ℓ^{eq} which vanishes for $T > T_c$ and is non-zero for $T < T_c$.

In our work we carried out the first quantitative computer simulations of the ordering process in a model binary alloy following quenching from a disordered (usually molten) state to a temperature $T < T_c$.

We analyzed our simulation data on the basis of the movement of domain walls separating regions (domains) whose ordering is different. The motion of the domain walls is such as to reduce their curvature. The theory predicts that the surface area per unit volume will decrease in proportion to $t^{-1/2}$. The results of our computer simulations gave strong support to the theory. We found the predicted $t^{-1/2}$ law during early periods following the quench, when the characteristic length ξ of the domains is small compared to the size of our

system. Also during this period the "staggered" structure function $S(k,t)$ is observed to scale in the way the theory suggests. When ξ becomes comparable to the size of the system, however, finite-size effects become important and there are large differences in the behavior of different samples in our simulation. Nevertheless, the late stages of the process can also be interpreted in terms of domain walls.

The physical situation here is quite different from that in a segregating alloy in which the order parameter is conserved. While there too, we found scaling behavior, the physical interpretation (and the scaling exponent) are quite different.

II. PHASE DIAGRAMS OF BINARY ALLOYS

We carried out extensive Monte Carlo computations of the coherent phase diagram (in the temperature-composition plane) of ordering binary alloys on a face-centered cubic lattice. Long- and short-range order parameters as well as ordering energies were obtained. We considered systems with both nearest and next nearest-neighbor interactions. Our results were compared with various theoretical predictions, particularly with the cluster-variation method which was found to be the most reliable. It gives fairly accurate results at stoichiometric composition. However, it too was found to fail in the more general case predicting a wrong topology of the phase diagram in the case of nearest-neighbor interaction. Our work

still stands now as the most reliable "experimental" phase
diagram for these systems.

III. POLYMERS

When a solution of macromolecules is sufficiently dilute,
the interactions between polymer chains can be neglected. A
good model for this system then consists of one chain in a sea
of solvent.

In our work we first investigated theoretically and via
computer simulations the statics and dynamics of a polymer chain
in a "good" solvent where only excluded volume effects are impor-
tant. We found that the distribution function for two beads
scales as the number of beads N to the power ν and that edge
effects are small. The dynamical correlation functions, such as
that of the end-to-end vector, scale as $N^{2\nu+1}$ with $\nu \simeq 0.6$.
The results of a dynamical lattice polymer model were shown to be
consistent with our results if one adjusts the time scales in
such a way that the center of mass diffuses at the same rate in
the two models. The relaxation of the stress tensor was found to
be quite similar to that of the Rouse model. Finally, it was
shown that edge effects are much more pronounced in the diffusive
motion of the individual beads, there being a skin comprising
about 40% of the total polymer, where bead motion is relatively
quicker.

Our results confirm the idea that for long chains the
degree of expansion due to excluded volume depends on the inter-

action range σ, on the number of links N, and on the link size b through a single variable $z \propto (\sigma/b)\sqrt{N}$.

We then studied polymer chains in a "poor solvent" with both repulsive and attractive interactions. Varying the temperature represents a polymer chain in solvents with differing degrees of solubility. We found that:

(a) At high temperatures, corresponding to good solvents, the dependence of the chain dimension R on the number of units N follows the same power law as does a chain with purely repulsive interaction; $R^2 \propto N^{2\upsilon}$, $\upsilon \simeq 0.6$.

(b) There is a temperature $\tilde{\theta}$ in the neighborhood of Flory's θ-temperature (at which the second virial coefficient of the interaction vanishes) where there is a linear relation between R^2 and N: $\tilde{\theta}-\theta$ depends on the "stiffness" of the chain.

(c) At lower temperatures the chain manifests a collapse which becomes more pronounced with increasing N.

There is overall qualitative agreement between our results, experiment, and a generalized form of Flory's theory although the behavior in cases b) and c) appears to depend on more details of the interaction than are taken into account in the latter.

We also carried out computer simulations on a polymer chain with excluded volume interactions in the presence of an external stretching force. For weak and moderate forces the response is

linear while for strong forces the behavior is nonlinear—
consistent with the non-Gaussian nature of the end-to-end
vector $\vec{R}$ distribution for large R. In the vicinity of the
θ-temperatures the onset of nonlinearity occurs at larger
forces.

Polymer chains with excluded volume interactions which
are confined within a slab of width D were also investigated.
We studied, in particular, $R^2(N, D)$, the mean square of the
end-to-end distance of a chain with N links. For large N and
fixed D, $R^2(N,D) \sim R_2^2(N)$, the squared end-to-end distance of a
chain constrained to a plane. We found $R_2^2(N) \equiv R^2(N,0) \propto N^{2\nu}$
with $2\nu = 3/2$ in agreement with the prediction of Flory. Letting
$R_3^2(N) \equiv R^2(N,\infty)$, the end-to-end distance for an unconstrained
three dimensional chain, we examined the cross-over scaling of
$R^2(N,D)/R_3^2(N)$ as a function $f(x)$ of $x \equiv D/R_3(N)$. For $x \lesssim 0.45$,
$f(x) \propto x^{-1/2}$, in agreement with predictions of Daoud and de Gennes.

IV. SIMPLE FLUIDS AND ELECTROLYTES

Our interest in the equation of state and correlation
functions of fluids dates back a long time and during the period
covered by this report we continued some work in this area. In
particular we investigated the structure of simple liquids as
well as that of electrolytes in the vicinity of a wall. (For
electrolytes the wall can represent a solid electrode and may
therefore carry an electric charge). Our work was two pronged:
a) we looked for and found some exact sum rules which gave exact
relations for suitably weighted integrals over the correlation

functions, b) we used various approximation schemes, e.g. Percus-Yevick integral equation, Mean Spherical Approximation and its generalizations, to compute the full density profile. The two approaches complemented each other in that we could use the sum rules for fixing certain parameters in the approximations.

Our results during this period included: a) an exact general expression for the contact value, $\rho(0)$, of the density profile of the fluid near a wall which could be charged, b) an exact result for the high field limit of the contact value, $q(0)$, of the charge profile, c) full density profiles in good agreement with machine calculations.

1. Equation of State of a Hard Core Fluid with Yukawa Tail, Jour. Molecular Physics, 35, 241 (1978). (With D. Henderson, E. Waisman and L. Blum).

2. Clusters, Metastability and Nucleation: Kinetics of First-Order Phase Transitions, Jour. Stat. Phys., 18, 39 (1978). (With M. Kalos, O. Penrose and A. Sur).

3. Growth of Cluster in a First-Order Phase Transition, Jour. Stat. Phys., 19, 6, 633 (1978). (With O. Penrose, J. Marro, A. Sur and M. Kalos).

4. Irreversible Thermodynamics for Quantum Systems Weakly Coupled to Thermal Reservoirs, Adv. Chem. Phys., 38, 109 (1978). (With H. Spohn).

5. Computer Simulation of the Dynamics of a Single Polymer Chain, Phys. Rev. Lett., 41, 5, 313 (1978). (With D. Ceperley and M. H. Kalos).

6. Towards a Rigorous Molecular Theory of Metastability, Studies in Stat. Mech., 7 (1979). (With O. Penrose).

7. Computer Simulation of the Time Evolution of a Quenched Model Alloy in the Nucleation Region, Phys. Rev. Lett., 43, 282 (1979). (With J. Marro and M. H. Kalos).

8. Monte Carlo Study of an Ordering Alloy on an FCC Lattice, Phys. Rev. Lett., 42, 9, 577 (1979). (With M. K. Phani, M. H. Kalos and C. C. Tsai).

9. Statistical Mechanics of Simple Fluids: beyond van der Waals, Physics Today, 33, 2 (1980). (With E. Waisman).

10. The Mean Spherical Approximation for a Yukawa Fluid Interacting with a Hard Planar Wall with an Exponential Tail, Jour. Molec. Phys., 39, 47 (1980). (With D. Henderson, L. Blum and E. Waisman).

11. An Exact Formula for the Contact Value of the Density Profile of a System of Charged Hard Spheres Near a Charged Wall, J. Electroanal. Chem., 102, 315 (1979). (With D. Henderson and L. Blum).

12. A Condition on the Derivative of the Potential in the Primitive Model of an Electric Double Layer, Jour. Chem. Phys., 72, (1980). (With L. Blum and D. Henderson).

13. Monte Carlo Studies of an fcc Ising Antiferromagnet with Nearest- and Next-Nearest- Neighbor Interactions, Phys. Rev. B, 21, 4127 (1980). (With M. Phani and M. Kalos).

14. Kinetics of an Order-Disorder Transition, Phys. Rev. Lett., 45, 366 (1980). (With M. Phani, M. Kalos and O. Penrose).

15. Monte Carlo Studies of Polymer Between Planes, Crossover Between Dimensionalities, Jour. de Phys., 41, 579 (1980). (With I. Webman and M. Kalos).

16. Excluded Volume Expansion of Polymer Chains. A Monte Carlo Study of Scaling Properties, Phys. Rev. B, 21, 5540 (1980). (With I. Webman and M. Kalos).

17. Book Review. Chain Polymers. Scaling Concepts in Polymer Physics. Pierre-Gilles de Gennes. Science, 208, 1140 (1980).

18. Dynamics of a Two-Dimensional Order-Disorder Transition, Phys. Rev. B, 24, 410 (1981). (With Paramdeep S. Sahni, Gregory Dee, J. D. Gunton, M. Phani, and M. Kalos).

19. Elastic Properties of a Polymer Chain, Phys. Rev. A, 23, 1, 316 (1981). (With I. Webman and M. H. Kalos).

20. Sum Rules for Inhomogeneous Coulomb Systems, Jour. Chem. Phys., 75, 2 (1981). (With Ch. Gruber and Ph. A. Martin).

21. Free Energy and Correlation Functions of Coulomb Systems, Erice Lecture Notes, Plenum Publishing (1981).

22. Computer Simulation of the Static and Dynamic Properties of a Polymer Chain, Macromolecules, 14, 1472 (1981). (With D. Ceperley and M. Kalos).

23. A Sum Rule for an Inhomogeneous Electrolyte, Jour. Chem. Phys., 75, 12 (1981). (With L. Blum, D. Henderson, C. Gruber, and P. Martin).

24. Monte Carlo Study of the Phase Diagrams of Binary Alloys with Face-Centered Cubic Lattice Structure, Acta Metallurgica, (1982). (With K. Binder, M. Phani and M. Kalos).

25. Dynamical Scaling of Structure Function in Quenched Binary Alloys, Acta Metallurgica, 30, 297 (1982). (With J. Marro and M. H. Kalos).

26. Properties of Two-Dimensional Polymers, Macromolecules, 15, 549 (1982). (With I. Webman, J. Tobochnik and M. Kalos).

Additional Publications

1. Dynamic Monte Carlo Renormalization Group, Phys. Rev. Lett., 46,1417 (1981). (By Jan Tobochnik, Sanjoy Sarker and Robert Cordery).

2. Physics of the Dynamical Critical Exponent in One Dimension, Phys. Rev. B, 24, 5402 (1981). (By Robert Cordery, Sanjoy Sarker and Jan Tobochnik).

3. Calculation of the Dynamical Exponent z for the Three-State
    Potts Model, Phys. Rev. B, 25, 4893 (1982). (By Jan Tobochnik
    and C. Jayaprakash).

4. Monte Carlo Renormalization-Group Analysis of the Antiferro-
    magnetic Three-State Potts Model on a Square Lattice, Phys.
    Rev. B, 25, 4890 (1982). (By C. Jayaprakash and J. Tobochnik).